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ULTRAFILTRATION OF RAW SEWAGE USING AN IMMOBILIZED ENZYME MEMBR--ETC(U)  
JUL 79 S S WANG, B DAVIDSON, C Y JENG N00014-77-C-0566

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ULTRAFILTRATION OF RAW SEWAGE  
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Ultrafiltration of raw sewage was performed using multiple- enzymes immobilized on non-cellulosic, ultrafiltration membranes. An increase of 12% in the permeate flux rate at quasi-steady state was observed due to the action of the immobilized enzymes. Enzymes were immobilized by physical sorption to minimize the		

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loss of ultrafiltration capability of the membrane, due to immobilization process. A mathematical model based on diffusive transport and enzymatic action was presented. A standard Marquardt algorithm and a fourth-order Runge-Kutta integration routine were used for estimation of the non-linear parameters in the model. Comparing data presented here to the data reported earlier on the ultrafiltration of NFDM (non-fat, dry milk), it was found that the enzyme-membrane has a longer half-life for the NFDM case than for the raw sewage case. Furthermore, the first-order enzyme decay rate is much faster in the multiple enzyme system used in raw sewage filtration than the single enzyme system used in the ultrafiltration of NFDM.

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## Introduction.

Ultrafiltration is a membrane process capable of separating macromolecular species ( $10^{-6}$  -  $10^{-2}$  mm in diameter) from solvent at high flux rate (2-10 cc/cm<sup>2</sup> hr.) by applying moderate pressure (10-100 psig). (Messinger, 1974.<sup>(1)</sup>) These characteristics make it a candidate process for sewage treatment, which has been investigated by Schatzberg, et al, 1973,<sup>(2)</sup> Harris, et al (1976),<sup>(3)</sup> and Harris, et al, 1977.<sup>(4)</sup> The main impediment to raw sewage ultrafiltration lies in the serious fouling of the membrane which decreases the permeate flux within a short period of operation.

Fouling of the membrane has been identified as the result of the gelling of macromolecular, or colloidal solutes in the membrane surface when the solutes are being concentrated by the concentration polarization process during ultrafiltration. Research on this phenomenon includes those by Brown, et al, 1971,<sup>(5)</sup> Kozinski, et al, 1972,<sup>(6)</sup> and Blatt, et al, 1970.<sup>(7)</sup>

The concentration levels at which solutes begin to gel differ widely. For example, protein solution tends to gel at 25 ~ 45 wt.%, while that for polysaccharides gel at below 1 wt.%. (Blatt, et al, 1970).<sup>(7)</sup> Raw sewage solids are reported to contain 40 ~ 60 wt.% protein, 20 ~ 50 wt.% carbohydrates, and 10 wt.% of oils and fats (Metcalf and Eddy, Inc., 1972).<sup>(8)</sup> The complexity of its composition makes the required method or device of removal or reduction of the gel-layer difficult.

One of the methods developed to remove the gel layer is by a fluid management technique. By this method, the back diffusive transport of solutes is increased so that the steady state permeate flux would stay

higher and the build-up of the gel layer lower (Blatt, et al, 1970).<sup>(7)</sup> One example is the design of a thin-channel, ultrafiltration module, which consists of passing the process stream through narrow channels of membrane (10-30 mils) at high velocities (5-25 ft/sec) (Porter, 1973).<sup>(9)</sup>

Ebner, et al, 1976,<sup>(10)</sup> reported a different method. By carefully creating a hydrodynamic drag force on the solute particles greater than the sliding friction force exerted by the membrane boundary, the concentration polarization can be counteracted. Filter aids can be added to magnify this effect.

Another approach is to immobilize enzymes on the membrane to hydrolyze the gel layer, thereby reducing the overall resistance to permeate flux. Dejmek, 1972,<sup>(11)</sup> bound trypsin to cellulose acetate to form a proteolytic active membrane, but no increases in permeate flux were found when the said membrane was used in ultrafiltration of proteinaceous solutions. On the other hand, Velincangil and Howell, 1978,<sup>(12)</sup> immobilized papain on an Amicon membrane. Using the immobilized papain-membrane to concentrate cheddar cheese whey, they obtained a 20% improvement in flux relative to the control after 78 hours of operation. A more remarkable improvement in flux was achieved by Gillespie, 1978.<sup>(13)</sup> An industrial grade protease was immobilized on a non-cellulosic tubular membrane (Abcor Inc., HFM) by a vacuum adsorption method. By filtering a non-fat dry milk solution with the immobilized enzyme membrane, flux enhancement of 93% over a period of 240 hours was observed.

Basically, the content of this paper is a continuation of Gillespie's work extended to the more complex raw sewage case and use of more sophisticated multi-enzymes, immobilized membrane systems.

## MATERIALS AND METHOD

### I. Ultrafiltration System.

Figure 1 is a sketch of the ultrafiltration unit in which raw sewage solution in the reservoir is circulating at 114 l/min through a tubular (152 cm x 2.54 cm $\phi$ )(5'x1"  $\phi$ ) non-cellulosic membrane (HFM-251-FN-0), obtained from Abcor, Inc., Wilmington, Massachusetts, with a molecular weight cutoff of 20,000. The system was operated at 50°C with a pressure drop of 276 kPag (40 psig) across the membrane. Both the circulating and the permeate streams are returned to the reservoir to approximate a total recycle mode. Permeate fluxes were compared between control (without enzyme) and prototype (with immobilized enzyme membrane) runs.

### II. Standardization of Sewage Solution.

It is expected that the larger particles in sewage solutions are more susceptible to hydraulic drag, and hence, are less likely to be incorporated into the growing gel-layer. Therefore, sewage samples were standardized before use by removing large particles through centrifuging at 8000 rpm for 20 minutes. The collected supernatant sewage solution, referred to as soluble sewage solution, was used for control and prototype runs.

### III. Initial Enzyme Screening Tests.

The ability of an enzyme to digest a gel-layer on a membrane was tested by a direct addition of the enzyme (10 grams) to be tested to the sewage solution in the reservoir (20 gallon) during a control run.

Enhancement of permeate flux following the addition indicates the ability of the enzyme to reduce the gel-layer thickness as a consequence of its hydrolytic activity.

#### IV. Enzyme Immobilization.

Because of the incompatibility of optimum pH's of the enzymes to be used, membrane prototype I was obtained by sequential immobilization of three enzymes, while membrane prototype II was obtained by simultaneous immobilization of two enzymes. In preparing membrane prototype I, 35.5 grams of Rhozyme<sup>(R)</sup> C2 and 54.5 grams of Rhozyme<sup>(R)</sup> HP-150 were centrifuged, mixed, diluted to 1500 cc, and adjusted to pH 5.0 by adding a dilute hydrochloric acid solution (0.1N). This solution was then drawn into the membrane tube chamber, which has been subjected to a vacuum of 25.6 in. Hg for one hour. The membrane was left soaking in the enzyme solution for one day, and then rinsed with water. Onto this membrane, 60 grams of Alcalase in 1500 cc of water (pH 7.23) was immobilized following the same vacuum-sorption technique.

In preparing membrane prototype II, 300 ml of Rhozyme<sup>(R)</sup> liquid protease #64 and 150 grams of Rhozyme<sup>(R)</sup> HP-150 were mixed, centrifuged, and adjusted to pH 4.5. The same vacuum-sorption technique was followed and the two enzymes were simultaneously immobilized.

## RESULTS AND DISCUSSION

Permeate flux data for control runs with 0.1% raw sewage solution, 0.1% insoluble sewage solution, and 0.1% and 0.03% soluble sewage solutions are plotted in Figure 2. The permeate flux-time curves shows that permeate flux decreases with increase in soluble sewage content in the solution, while insoluble sewage does not have the same effect as the soluble sewage at the same concentration level. These results suggest that the gel-layer is mainly composed of the soluble sewage.

An enzyme is identified as active toward the gel-layer if the direct addition of it into an operating ultrafiltration systems causes an increase in permeate flux. Table 1 lists the enzymes tested and the result of their activities toward sewage gel-layer. The response of the permeate flux after the addition of an active enzyme follows a pattern of rising and falling back to the original level during the screening test. Figure 3 illustrates this rising and falling effect. This effect is further investigated by adding one part of an enzyme mixture into the ultrafiltration system and saving another part of it for a second addition. While the first addition of the enzyme mixture gave the rising and falling of permeate flux, the second addition of the same enzyme mixture did not, as shown in Figure 4. One explanation of it is that enzymes are specific to substrates. First addition of an enzyme may clear away all the substrate and leave the system substrate free and, therefore, inert to the second addition of the same enzyme.

Flux enhancement in prototypes I and II over control is shown in Figures 5 and 6. Time averaged permeate flux improvements are listed in Table 2. While direct addition of enzyme into the ultrafiltration

system provides the breakdown of the gel-layer at the circulating stream side, immobilized enzyme would attack the gel-layer from the membrane side.

Our experience with ultrafiltration of non-fat dry milk solution in a protease immobilized membrane system showed a 90% increase in flux for the first 50 hours of operation (Gillespie, 1978).<sup>(13)</sup> By contrast, results on the ultrafiltration of soluble sewage solution only showed a 12% increase in flux when the prototype was compared to the control for the same time period of operation.

Since sewage is a much more complex substrate than NFDM solution, it is believed that with the proper selection and blending of enzymes to be immobilized on the ultrafiltration membrane, a better result can be expected. Although eight different enzymes were screened in this study, more screening tests on different sources of enzymes are still needed to achieve an optimal performance. The results of this study definitely establish the scientific basis on which to justify the continued search for process improvement through better enzyme selection.

## MATHEMATICAL MODELING AND PARAMETER IDENTIFICATION

### I. Membrane Permeability.

According to Blatt, et al., 1970,<sup>(7)</sup> the transport of solvent across a membrane with molecular weight cut-off of 500, or above, can be approximated as a viscous flow through micropores in the membrane; i.e.,

$$J = \frac{\Delta P_m}{R_o} \quad (1)$$

where  $J$  = Permeate flux of solvent

$\Delta P_m$  = Hydraulic pressure drop across membrane, with or without enzyme immobilized.

$R_o$  = Hydraulic resistance of membrane, with or without enzyme immobilized.

### II. Gel-layer Permeability:

The growing gel-layer is assumed to be of uniform density or concentration,  $C_G$ , and hydraulic permeability. Solvent flux across the gel-layer is also approximated as a viscous flow through micropores:

$$J = \frac{\Delta P_G}{K_G \delta} \quad (2)$$

where  $\Delta P_G$  = Hydraulic pressure drop across the gel-layer

$K_G$  = Specific hydraulic resistance of the gel-layer

$\delta$  = Thickness of the gel-layer

### III. Mass Transfer Through a Diffusive Layer:

A material balance over a control volume in the diffusive layer (Figure 7) gives the following differential equation for the solute:

$$\frac{\partial}{\partial r} \left( D \frac{\partial C}{\partial r} - \frac{\partial}{\partial r} [(J + N') \cdot C] \right) = \frac{\partial C}{\partial t} \quad (3)$$

where  $N'$  = Volumetric flow of solute

$D$  = Apparent diffusivity of solute

$C$  = Solute concentration

Since in ultrafiltration,  $N'$  is far less than  $J$ ,  $(J + N')$  is approximated by  $J$ . Furthermore, by assuming quasi-steady state, or  $\frac{\partial C}{\partial t} = 0$ , equation (3) is integrated once to obtain:

$$J \cdot C - D \frac{dC}{dr} = N \quad (4)$$

where  $N$  = Solute flow in the diffusive layer

Equation (4), together with the boundary conditions is integrated:

$$r = 0 \quad C = C_B \quad (5)$$

$$r = \theta \quad C = C_G \quad (6)$$

where  $C_B$  = Solute concentration in bulk flow

$C_G$  = Solute concentration in the gel-layer

$\theta$  = Thickness of the diffusive layer

Thus,  $N$  can be solved in terms of  $\theta$ ,  $D$ ,  $C_B$ ,  $C_G$ , and  $J$  as:

$$N = J \cdot C_G \left( \frac{C_B}{C_G} - e^{-\frac{\theta}{D} \cdot J} \right) / \left( 1 - e^{-\frac{\theta}{D} \cdot J} \right) \quad (7)$$

#### IV. Growth of the gel-layer:

The gel-layer is thickened by the solute transported from the

diffusive layer and diminished by the solute digested away by the immobilized enzyme. The effective rate of gel-layer digestion is given by a zero-order reaction kinetic approximation to the Michelis-Menten rate law with an exponential time decay factor. Therefore,

$$\frac{d\delta}{dt} = \frac{1}{C_G} \left( N - K_1 e^{-K_2 t} \right) \quad (8)$$

where  $\delta$  = Thickness of the gel-layer

$K_1$  = Zero order rate constant of the immobilized enzyme

$K_2$  = First-order decay constant of the immobilized enzyme

#### V. Transient Model of the System.

Equations (1) and (2) represent processes whose resistances are in series. Hence, they can be combined to give

$$J = \frac{\Delta P}{R_o + K_G} \quad (9)$$

where  $\Delta P = \Delta P_M + \Delta P_G$ , the total pressure drop

Equations (7), (8), and (9) give the complete model which describes the transient behavior of the permeate flux and the growth of the gel-layer during steady recycle operation of the ultrafiltration system. By combining equations (7) ~ (9), a relationship for permeate flux,  $J$ , is obtained in terms of the parameters of the ultrafiltration system:

$$\frac{dJ}{dt} = \frac{-K_G J^2}{\Delta P} \left\{ J \cdot \left[ \left( \frac{C_B}{C_G} - e^{-\frac{\theta}{D} \cdot J} \right) / \left( 1 - e^{-\frac{\theta}{D} \cdot J} \right) \right] - \frac{K_1}{C_G} e^{-K_2 t} \right\} \quad (10)$$

with an initial condition of  $t = 0$ ,  $J = \frac{\Delta P}{R_0}$ , and  $K_1 = 0$  for the control case.

#### VI. Steady State Permeate Flux:

At steady state,  $\frac{dJ}{dt} = 0$ , equation (10) can be solved for the permeate flux,  $J_{ss}$ , for the control case ( $K_1 = 0$ ):

$$J_{ss} = \frac{D}{\theta} \ln \frac{C_G}{C_B} \quad (11)$$

Equation (11) is exactly the same as that given by Blatt, et al., 1970.<sup>(7)</sup>

#### VII. Parameter Identification:

The optimal values of the unknown parameters in the model were obtained by using a Marquardt algorithm and a Fourth-Order Runge-Kutta integration for equation (10). The objective function is

$$\text{Min } \sum_i (J_{i,\text{model}} - J_{i,\text{exp}})^2 \quad (12)$$

An initial estimate of  $\frac{D}{\theta}$  is obtained from the following equation given by Porter (1973)<sup>(9)</sup>

$$\frac{D}{\theta} = 0.23 \frac{(U)^{0.8} (D)^{0.67}}{(d)^{0.2} (v)^{0.47}} \quad (13)$$

where  $U$  = flow velocity

$v$  = kinematic viscosity of solvent

$d$  = hydraulic diameter

$D$  = diffusivity of solute

A physically realistic diffusivity of sewage solute is taken to be  $1.0 \times 10^{-7} \text{ cm}^2/\text{sec}$ . The corresponding value of  $\frac{D}{\theta}$  from equation (13) is thus calculated to be 1.8 cm/hr.

It is noted that  $C_G$  and  $\frac{D}{\theta}$  are correlated, as indicated in equation (11). These constraints are used to aid in establishing proper initial values for  $C_G$  and  $\frac{D}{\theta}$  during the parameter estimation routine.

Table (3) lists the parameters computed from the Marquardt algorithm after exhaustive iteration. Figure 8 illustrates a good agreement between the observed experimental data and the simulated values.

#### Gel-layer Thickness under Scanning Electron Microscope.

In previous experimental work performed by Gillespie, 1978,<sup>(13)</sup> on the ultrafiltration of non-fat dry milk in our laboratory, it was demonstrated that Rhozyme<sup>(R)</sup> P-53 was effective in permeate flux enhancement. Data from that work were simulated by the above described model and algorithm. The parameters are listed in Table 3 and simulated curves plotted in Figure 9. The calculated gel-layer thickness after 30 hours of operation for the control run is 400 $\mu$ . Such a gel-layer thickness corresponds to a permeate flux of  $2.66 \text{ cm}^3/\text{cm}^2 \text{ hr}$ . under a 276 kPag (40 psig) driving force. To check the validity of the calculated gel-layer thickness, a direct measurement of it was carried out by taking pictures of gel-layer samples under a Scanning Electron Microscope. The samples were prepared by using membranes fitted into an Amicon Diaflo<sup>(R)</sup> unit (Model 402) with 0.1 wt.% solution of non-fat dry milk under a pressure of 276 kPag (40 psig). As permeate flux came down to  $1.4 \text{ cm}^3/\text{cm}^2 \text{ hr}$ ., the operation was terminated and the membrane was taken out, rinsed,

and air dried. This dried gel-layer, under a Scanning Electron Microscope, was measured to be around 100 $\mu$  in thickness, Bearing in mind that the gel-layer shrinks after drying, the authors believe that the calculated thickness is in the right order of magnitude. This conclusion lends confidence to the method used to estimate the parameters from the proposed model.

A sample of dried gel layer of sewage on a tubular membrane was also observed under a Scanning Electron Microscope, and the thickness of it was estimated to be 40 ~ 50 $\mu$ . The sample was obtained from Naval Ship Research and Development Center, Annapolis, Maryland, using a similar prototype system.

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TABLE 1

Enzymes used in screening test

Enzyme Name*	Lot No.	Source	Test Result
Pectinol R-10	3-2437	Rhom & Haas	-
Liquid Protease	64 3-29016	Rhom & Haas	+
Alcalase	M2-3207	Novo Lab.	+
Cellulase	13C-9510	Sigma	-
Rhozyme HP-150	3-0007	Rhom & Haas	+
Pectinol 60 G	3-32077	Rhom & Haas	-
Rhozyme P-53	3-2358	Rhom & Haas	+
Rhozyme CL		Rhom & Haas	+

---

\* Trade Name

TABLE 2

Flux Improvement by Immobilized Enzyme on Membrane

<u>Time Period (hr)</u>	<u>Control I *</u>	<u>Prototype I *</u>	<u>Improvement (1%)</u>
0-5	4.4	5.4	21
0-10	4.2	5.0	19
0-15	4.1	4.7	16
0-50	4.0	4.4	12

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<u>Time Period (hr)</u>	<u>Control II *</u>	<u>Prototype II *</u>	<u>Improvement (%)</u>
0-5	4.7	5.4	14
0-10	4.5	5.0	12
0-15	4.3	4.8	11

---

\* Time averaged flux in c.c./cm<sup>2</sup> hr.

TABLE 3

Parameters for Sewage and NFDM Ultrafiltration Systems

	Sewage	NFDM
$C_G$ (gm/cm <sup>3</sup> )	0.118	0.313
$\frac{D}{\theta}$ (hr/cm)	1.43	1.90
$K_G$ (psi-hr/cm <sup>2</sup> )	175.4	261.0
$\delta^*$ (cm)	0.056	0.04
$K_1$ (cm/hr)	0.0034	0.0066
$K_2$ (hr <sup>-1</sup> )	0.027	0.0072
$t_{1/2}^{**}$ (hr)	26.0	95.4

\* Gel-layer thickness for control runs after 47 hours for sewage  
and 30 hours for NFDM.

\*\* Apparent half life of the enzyme immobilized on membrane.

NOTATION

- $C$  = solute concentration,  $\text{gm/cm}^3$   
 $C_B$  = solute concentration in bulk flow,  $\text{gm/cm}^3$   
 $C_G$  = solute concentration in gel-layer,  $\text{gm/cm}^3$   
 $D$  = apparent diffusivity of solute,  $\text{cm}^2/\text{hr}$   
 $d$  = hydraulic diameter,  $\text{cm}$   
 $J$  = flux of solvent,  $\text{c.c./cm}^2\text{hr.}$   
 $J_{ss}$  = steady state permeate flux,  $\text{c.c./cm}^2\text{hr.}$   
 $K_G$  = specific hydraulic resistance of the gel-layer,  $\text{psi-hr/cm}^2$   
 $K_1$  = zero order rate constant of the immobilized enzyme,  $\text{gm/cm}^2\text{hr.}$   
 $K_2$  = first order decay constant of the immobilized enzyme,  $\text{hr}^{-1}$ .  
 $N$  = solute flow in diffusive layer,  $\text{gm/cm}^2\text{hr.}$   
 $N'$  = volumetric flow of solute,  $\text{c.c./cm}^2\text{hr.}$   
 $P$  = total pressure drop,  $\text{psig.}$   
 $P_G$  = pressure drop across gel-layer,  $\text{psig.}$   
 $P_M$  = pressure drop across membrane,  $\text{psig.}$   
 $R_o$  = Hydraulic resistance of membrane,  $\text{psi-hr/cm.}$   
 $r$  = distance perpendicular to membrane,  $\text{cm.}$   
 $U$  = bulk flow velocity of circulating stream,  $\text{cm/sec.}$   
 $\theta$  = thickness of diffusive layer,  $\text{cm.}$   
 $\delta$  = thickness of gel-layer,  $\text{cm.}$   
 $\nu$  = kinematic viscosity of solvent,  $\text{cm}^2/\text{sec.}$

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### CONCLUSIONS

(1) As shown by the 12% increase in flux for the prototype system over the control, and considering the cost of enzymes used (estimated to be ten dollars for one immobilization procedure), it is a definite process advantage to use immobilized enzymes in ultrafiltration applications. The high performance of immobilized protease in ultrafiltration of non-fat dry milk as compared to that of the multiple immobilized enzymes presented in this study indicated that the proper selection of enzymes and optimum blending of them would allow improvements on the performance of an enzyme-ultrafiltration system for filtering complex substrates such as sewage solution.

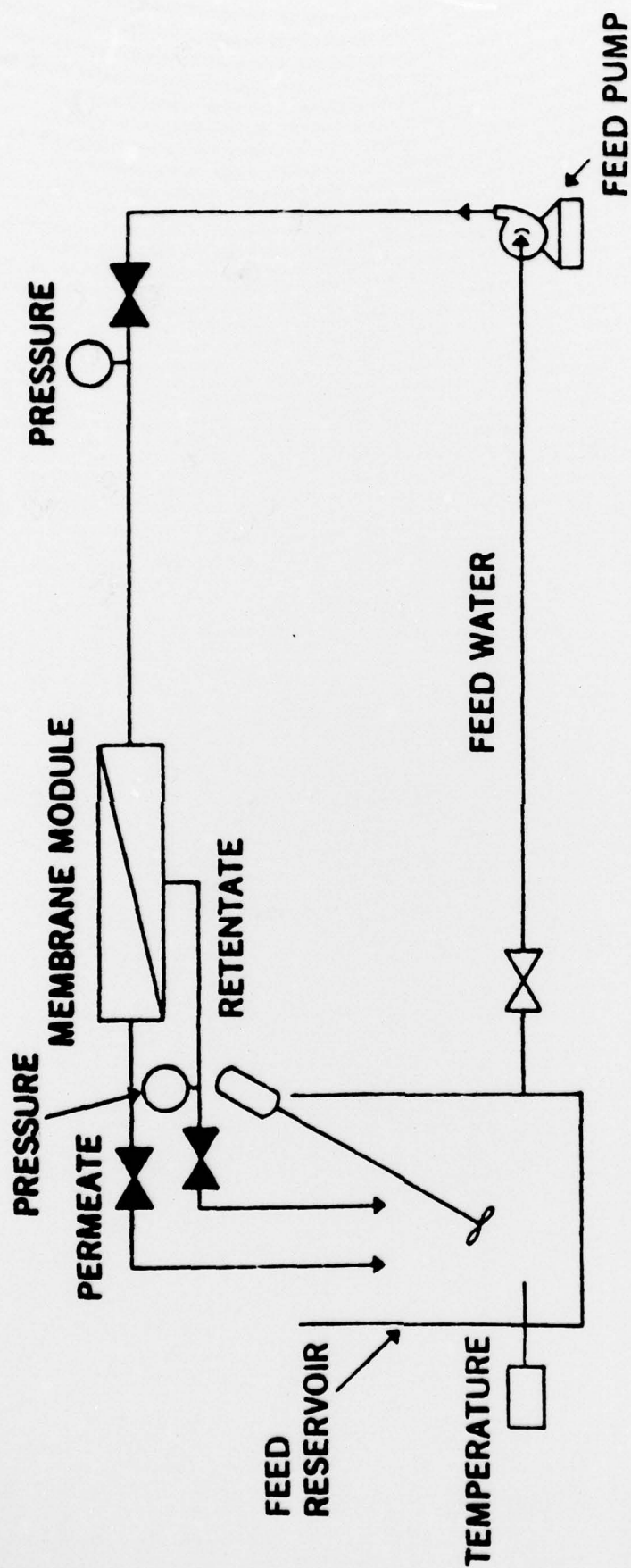
(2) Experimental measurements of the gel-layer thicknesses, using a scanning electron microscope, have produced results which correlate well with those predicted from simulated results using estimation theory and a dynamic transient flux model. This rather fortuitous finding lends real encouragement to the method used to estimate system parameters from observed data for the proposed model.

#### ACKNOWLEDGMENTS

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### FIGURE LEGENDS

- Figure 1. Schematic Diagram of the Prototype Ultrafiltration System.
- Figure 2. The effect of substrate concentrations on the permeate rates of ultrafiltration.
- Figure 3. Screening of potential enzymes for the enhancement of ultrafiltration rates.
- Figure 4. Permeate flux responses to two additions of one enzyme mixture.
- Figure 5. The effect of immobilized enzymes on the permeate flux rate of ultrafiltration of prototype I.
- Figure 6. The effect of immobilized enzymes on the permeate flux rate of ultrafiltration of prototype II.
- Figure 7. Boundary layers of ultrafiltration showing concentration and pressure changes along the direction of permeate flux.
- Figure 8. Experimental data and simulated curves of sewage ultrafiltration.
- Figure 9. Experimental data and simulated curves of the non-fat dry milk ultrafiltration.



**FIGURE 1 SCHEMATIC DIAGRAM  
OF THE PROTOTYPE ULTRA FILTRATION SYSTEM**

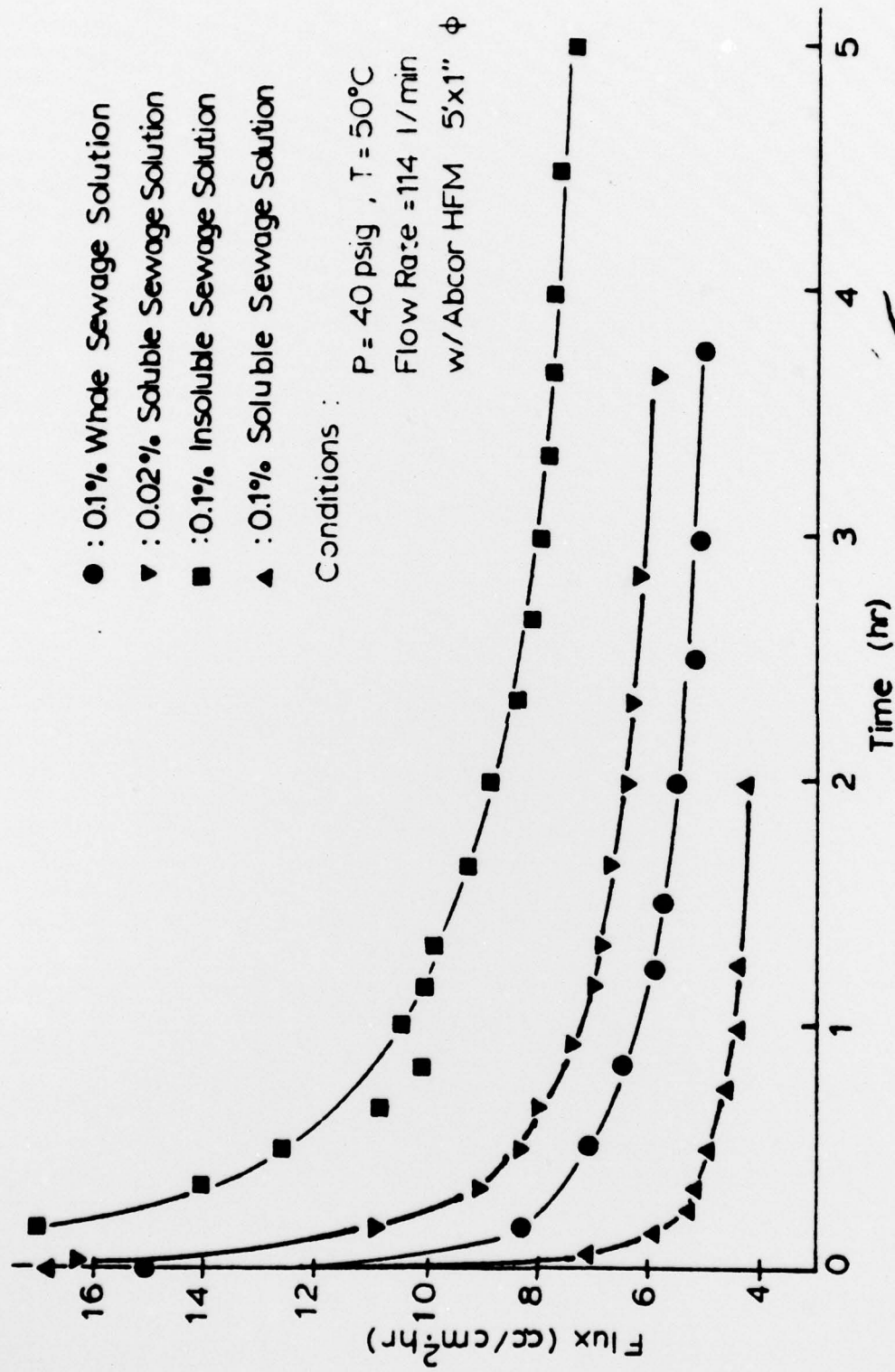


Figure 2. The effect of substrate concentrations on the permeate rates of ultrafiltration.

0.1% Soluble Sewage Solution

↓: Addition of Enzymes

1. Rhozyme HP-150

2. Rhozyme CL

3. Alcalase

4. Rhozyme R-10

5. Rhozyme P-53

Conditions :

P = 40 psig , T = 50°C

Flow Rate = 114 l/min

w/ Abcor HFM 5'x1"  $\phi$

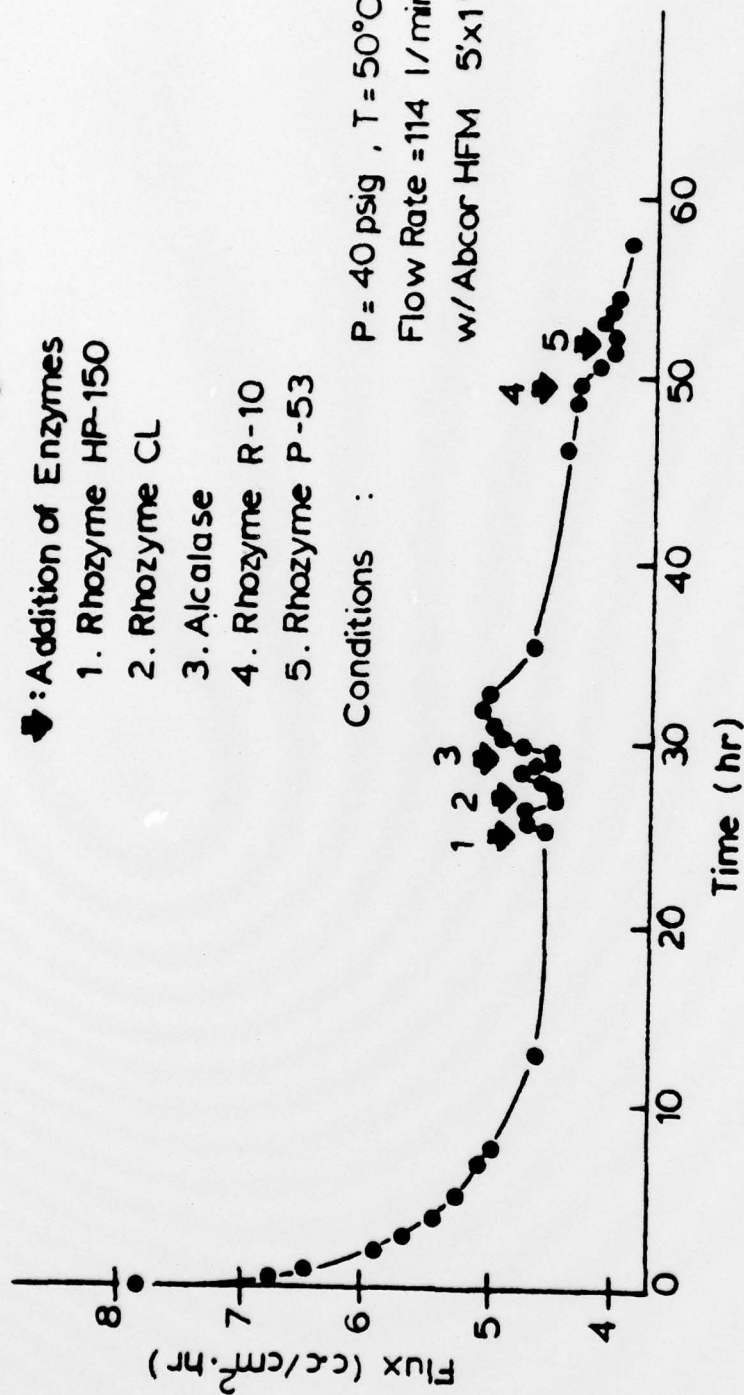


Figure 3. Screening of potential enzymes for the enhancement of ultrafiltration rates.

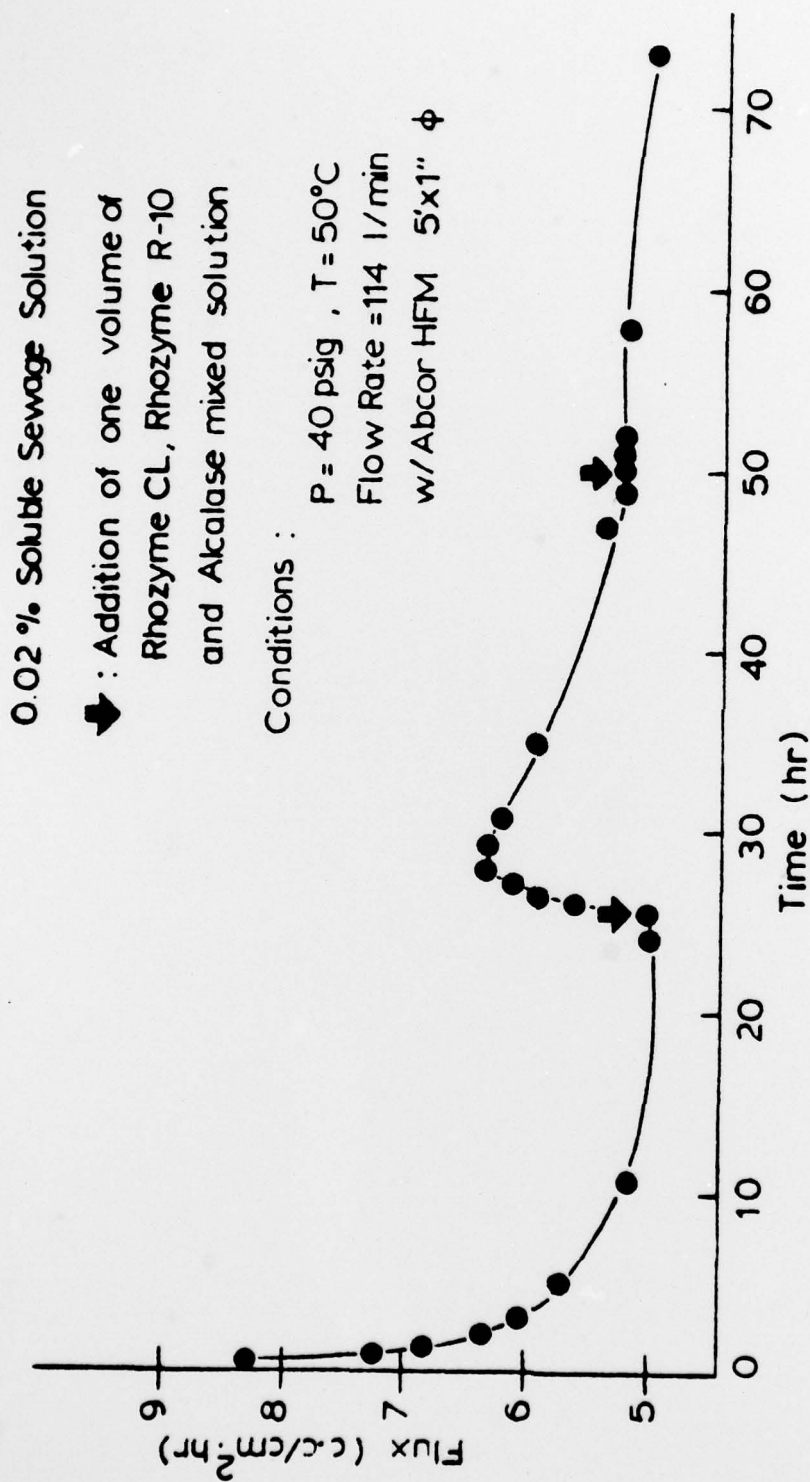


Figure 4. Permeate flux responses to two additions of one enzyme mixture.

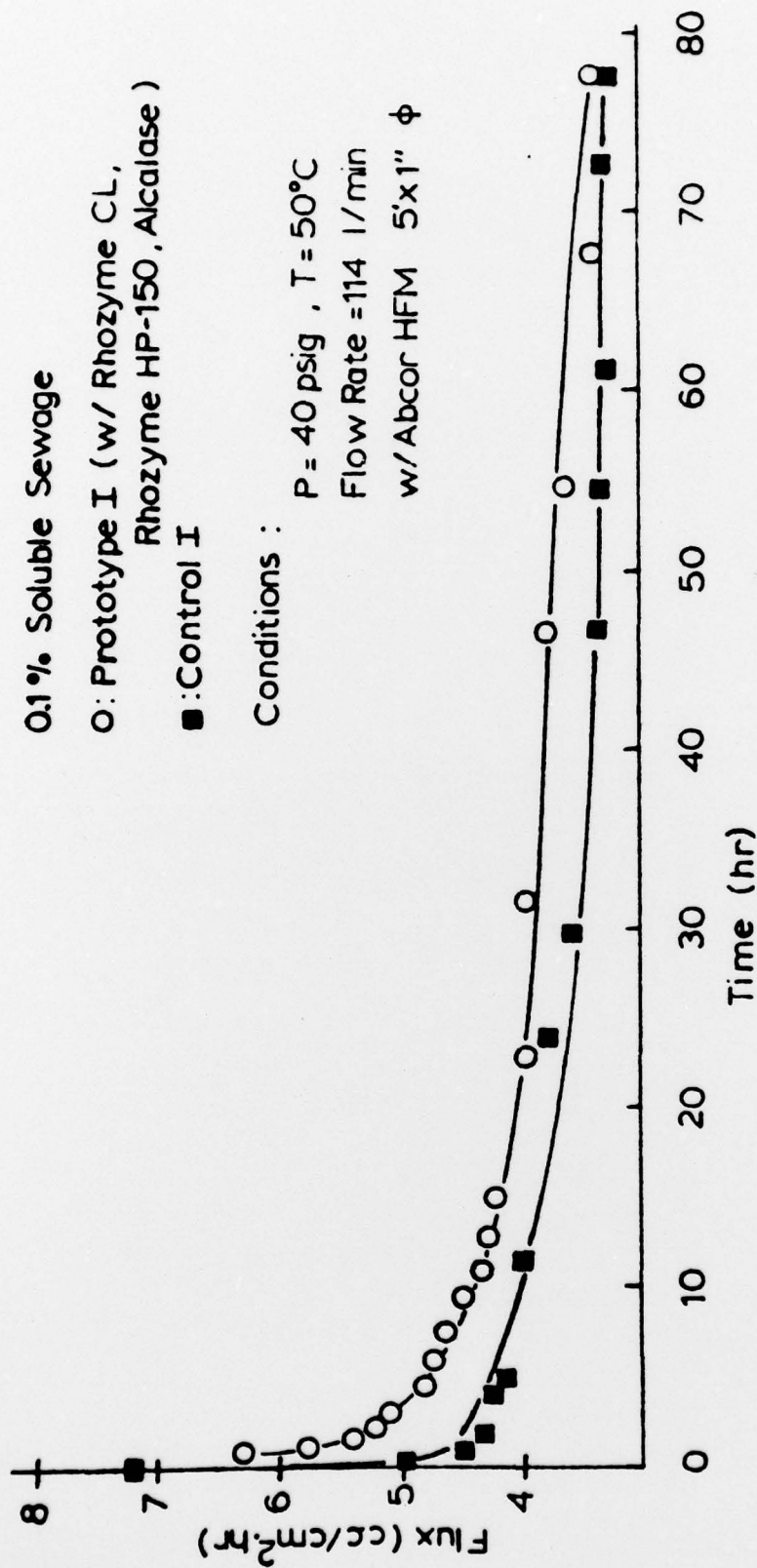


Figure 5. The effect of immobilized enzymes on the permeate flux rate of ultrafiltration of prototype I.

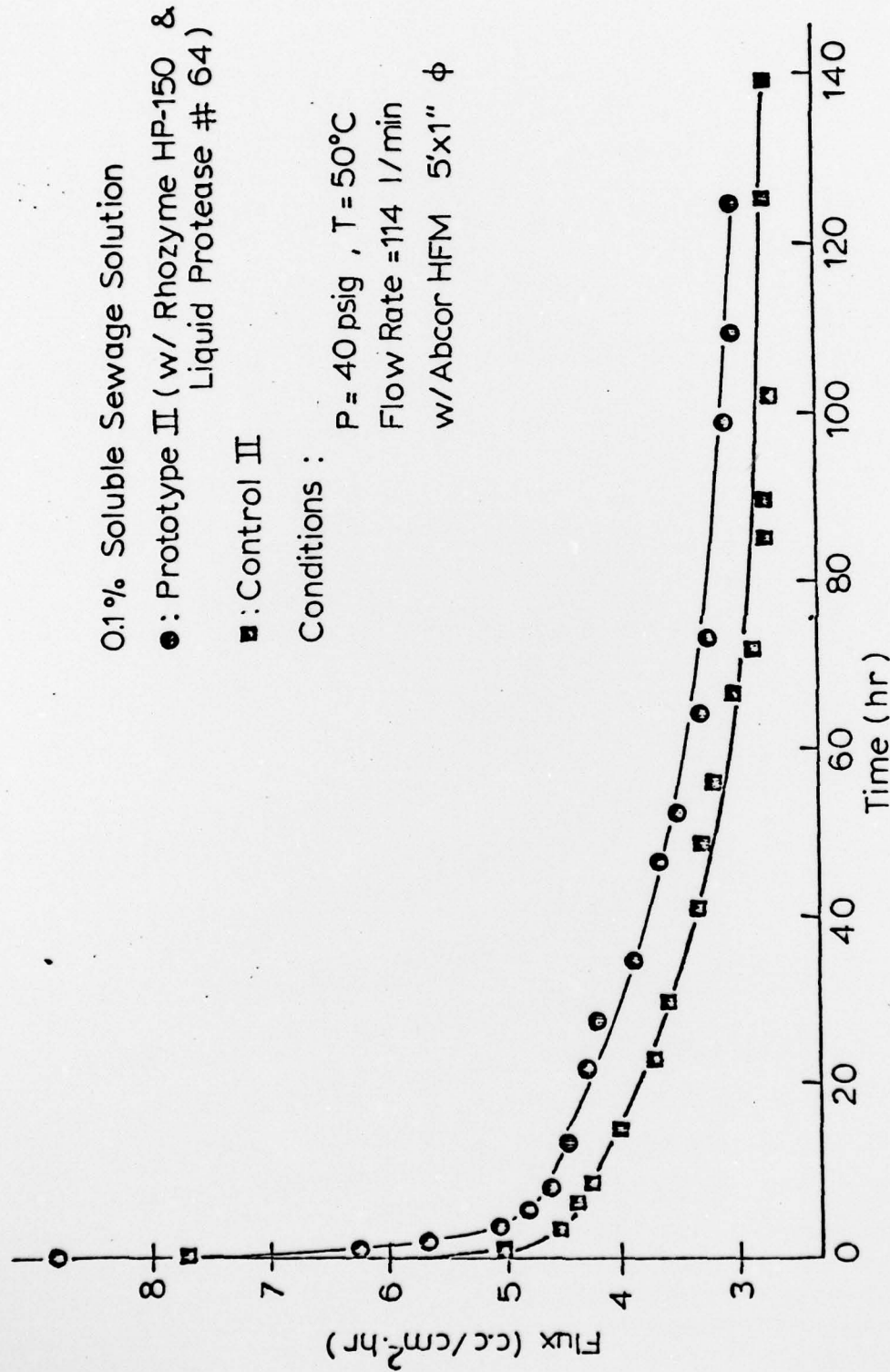


Figure 6. The effect of immobilized enzymes on the permeate flux rate of ultrafiltration of prototype II.

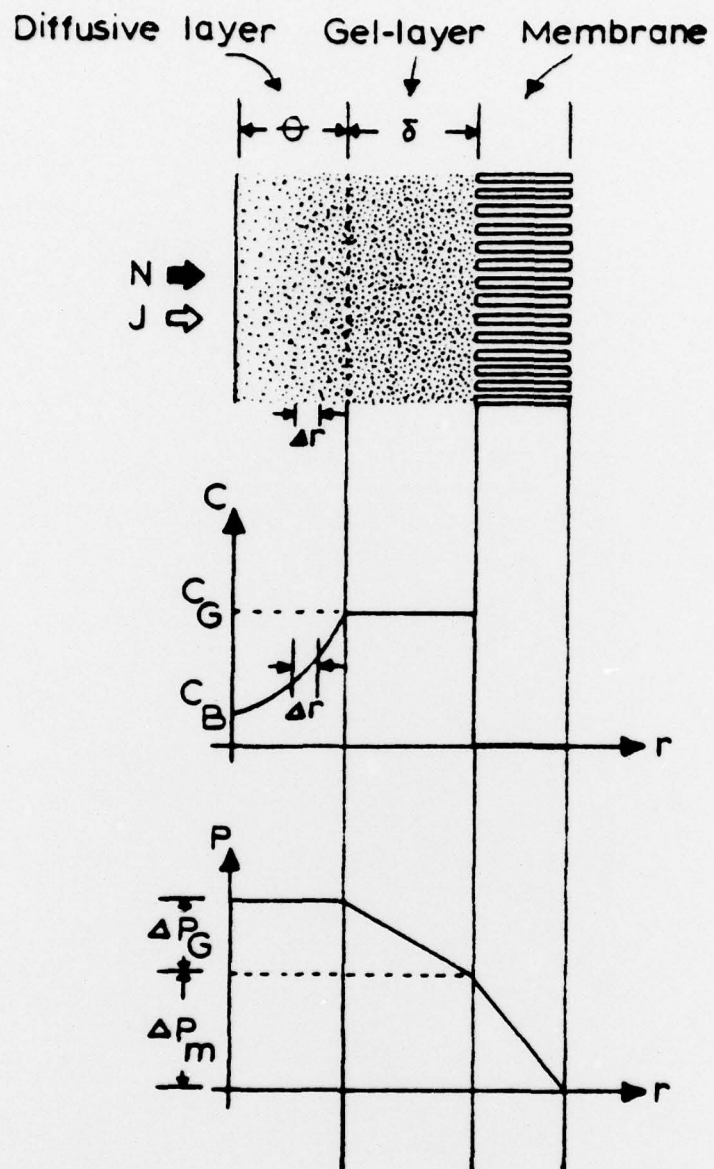


Figure 7. Boundary layers of ultrafiltration showing concentration and pressure changes along the direction of permeate flux.

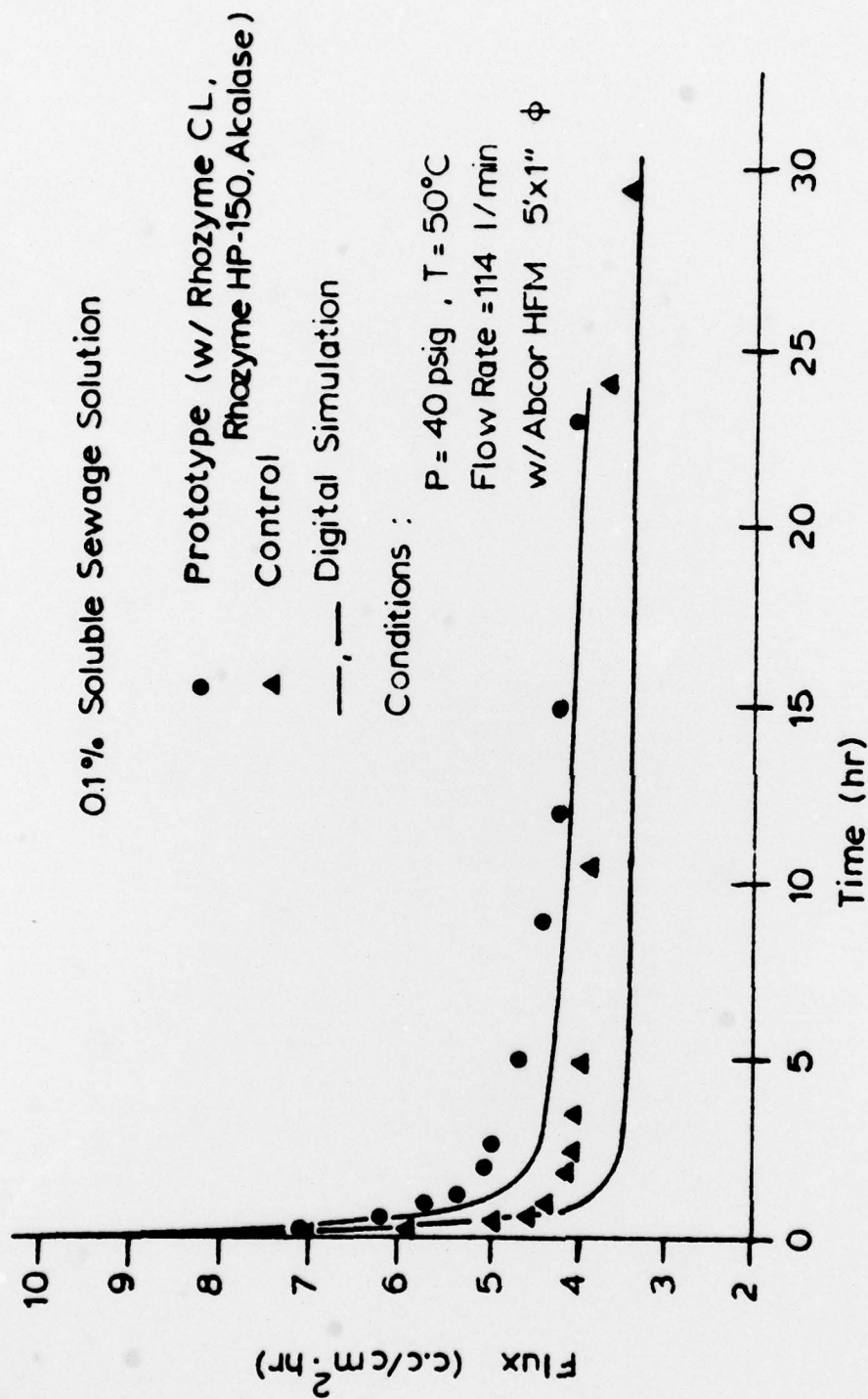


Figure 8. Experimental data and simulated curves of sewage ultrafiltration.

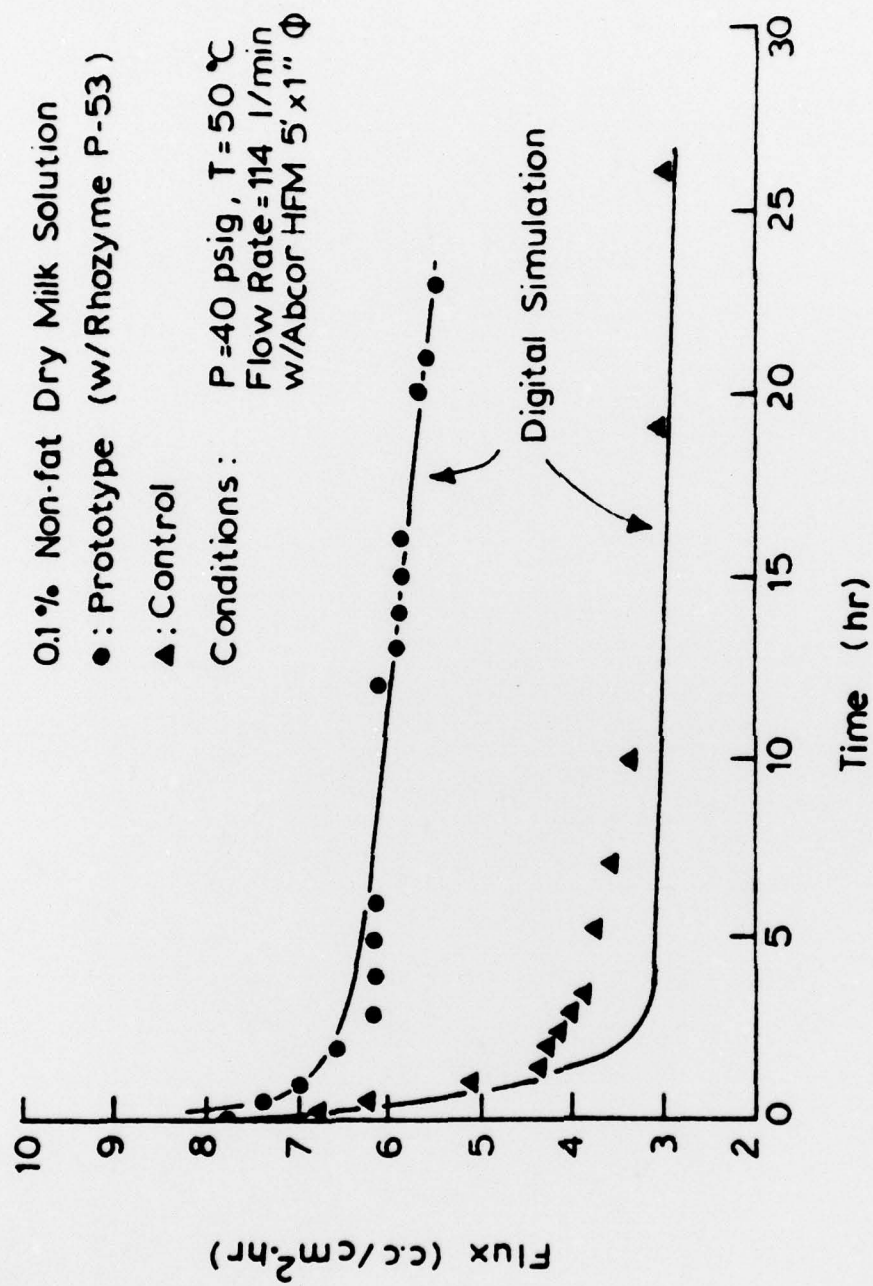


Figure 9. Experimental data and simulated curves of the non-fat dry milk ultrafiltration.